(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
1 August 2002 (01.08.2002)

PCT

(10) International Publication Number
WO 02/059394 A2

(51) International Patent Classification[7]: C23F 13/16

(21) International Application Number: PCT/IB02/00202

(22) International Filing Date: 23 January 2002 (23.01.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
AN2001A000005 26 January 2001 (26.01.2001) IT

(71) Applicant *(for all designated States except US)*: **THERMOWATT S.P.A.** [IT/IT]; 21, Via San Giovanni Battista, I-60011 Arcevia (IT).

(72) Inventor; and

(75) Inventor/Applicant *(for US only)*: **FIORONI, Fausto** [IT/IT]; Thermowatt S.p.a., 21, San Giovanni Battista, I-60011 Arcevia (IT).

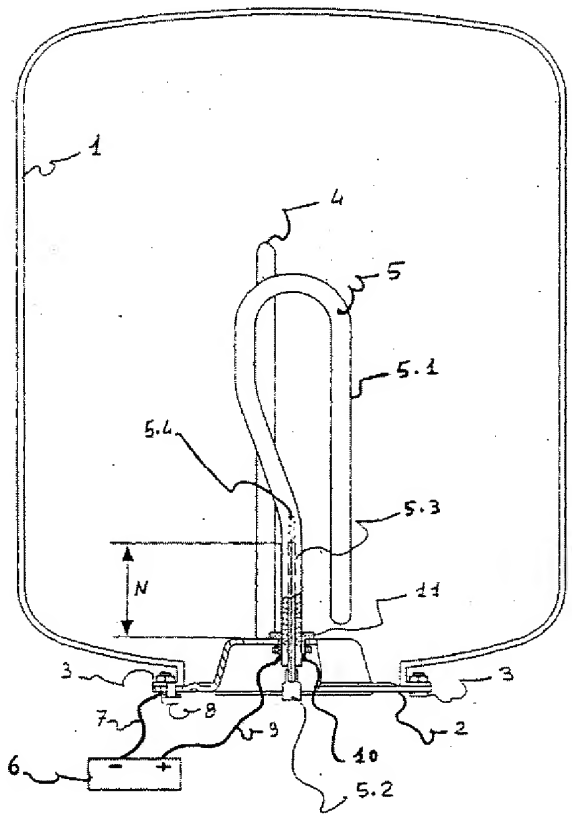
(74) Agent: **GENTILI, Enrico**; Mar. Bre S.r.l., 1, Viale Aristide Merloni, I-60044 Fabriano (IT).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent

[Continued on next page]

(54) Title: MEANS FOR PROTECTING FROM CORROSION METALLIC TANKS CONTAINING LIQUIDS TO BE HEATED; WATER HEATERS IN PARTICULAR



(57) Abstract: The present invention concerns devices apt to protect from corrosion metallic tanks (1) containing liquids to be heated, water heaters in particular. According to the invention, a non-consumable type electrode, for cathode protection in particular, consists of the armour (5.1), preferably in titanium or its alloys, of one or more armoured electric resistances (5). Part of the surface of the said armour (5.1) can be subjected to a treatment that prevents the supply of current. The advantages of the invention include the constructional simplification of the electrodes and the fact that no scale deposits are formed on the surfaces of the armours (5.1) used as electrodes.

WO 02/059394 A2

(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

MEANS FOR PROTECTING FROM CORROSION METALLIC TANKS CONTAINING LIQUIDS TO BE HEATED, WATER HEATERS IN PARTICULAR

DESCRIPTION

It is the object of the present invention to provide a device for protecting from corrosion the metallic tanks for heating water by means of electric resistances, specifically for protecting water heaters.

The electric resistances generally used for heating water in electric water heaters are armoured, consisting of a metallic tubular element, the armour, which contains a spiral of a resistive electric filament; in general, it acts as a dielectric of the roll-pressed magnesium oxide in order to keep the spiral resistance in the middle of the tubular element forming the armour. Several metallic alloys fitted for undergoing the working processes required by the constructional technology, permanent sets in particular, are fit to act as armour as well as to endure the working temperatures; in the case of resistances plunged in water or in other liquid means, the metallic alloy must have the required resistance to corrosion. The armour of the electric resistances used in tank water heaters is in copper alloy or in stainless steel.

A frequent problem in this type of electric resistances supplying a high thermal power (8.5 W/cm^2), is the scale deposit that forms quite quickly on the surface, especially with hard water; the layer of scale heats the armour and the latter boils the water through contact, with ensuing noise and, in the long run, breakage of the resistance.

In electric water heaters, as in similar equipment containing consumption water to be heated, another important problem consists of the corrosion to which the internal surface of the water tank is subjected if it is metallic. The corrosion process due to the contact between water and the metallic alloy increases with the water temperature.

The phenomenon is also present in water heaters and in other metallic tanks with internal

surface protected by an electrically insulating layer in synthetic or vitreous material; actually, defects and porosity in such protective layers are inevitable; if there are no proper electrochemical means of protection, the piercing of the metallic wall is even quicker than in zinc-plated tanks, because the process is completely concentrated on the small areas in which the protective layer is flawed.

To overcome or at least to clearly reduce the phenomenon of corrosion, apart from applying a deposit of protective material on the metallic tank, two methods of electric protection are mainly used: an anodic and a cathode method.

The anodic protection occurs by bringing the metallic structure of the water heater to a potential value higher than an electrode, which acts as a cathode, up to a passivation value; in this case the structure to be protected acts as an anode.

The drawback of the anodic protection system is the need to apply, by means of a proper device, a specific voltage value; if such a value is not duly observed the walls of the structure to be protected are not protected from passivation and the corrosion quickly produces its destructive effect. Therefore, considering the need to carefully control the voltage value, the anodic protection does not seem to be the most suitable one for sanitary water heater equipment at home while it can be used in big-sized tanks and structures, since it uses very little current.

The cathode protection is carried out by making the potential of the metallic structure of the water heater lower than that of the aggressive means. In this kind of protection, the direct current circulates, through the tank water, from an anode to the walls of the tank of the water heater, which acts as a cathode.

The element acting as an anode can be a metal or an alloy with an electrochemical potential considerably higher than that of the metallic structure to be protected; such anode is called sacrificial because it is subjected to a gradual wear when the water heater is working and must be regularly replaced. The drawback of this simple protection is that, if the replacement does not occur, the corrosion begins quickly.

The current can also circulate by using an external generator, i.e. an impressed current protection system. The clamp of the generator is electrically connected to the metallic mass to be protected while the other one is connected to the electrode, which is otherwise electrically insulated as to the metallic mass.

This kind of protection is getting more and more widespread to the detriment of the sacrificial anodes but all the solutions put forward until now present drawbacks that can be attributed mainly to high costs, to a persistent difficulty in ensuring a uniform distribution of the impressed current, and also to a certain arduousness of the electrode assembly operations. The electrode is manufactured in various materials electrically conductive and difficult to corrode, e.g. titanium bars or its alloys. The known physical or chemical means for protecting one part of the external surface of the said bars are used for the portion of the surface no to supply current and other physical or chemical means for facilitating the current supply from other areas of the same surface; the purpose of this is to determine at best, as well as with the shape and the position of the electrode, the areas of the metallic tank towards which the current must be supplied.

Several types of electrodes manufactured for water heaters or similar elements are known; the most recent ones are examined below.

The previous document EP 0 771 889 presents, as a support to an electrode, the tubular element forming the holding sheath of the thermostat sensors. The seal and electric insulation between electrode and tubular element is carried out by a special support.

The Italian patent request n. AN 99A000003 presents interesting characteristics of electric connection between electrode and water heater tank that occurs without the need of electric cables at least for the part passing between the electrode and the external surface of the said water heater.

The said document considers also an electrode that cannot be corroded, full, tuned on and electrically connected to the end of the holding sheath of the thermostat sensors. The sheath is fixed to the flange by means of an insulating joint in order to prevent the electric contact between the electrode and the tank to be protected. Since the said tubular support is made of a metallic material that can be corroded, it must be protected efficiently for its whole length, as well as the point in which the electrode is inserted in the said sheath.

The dual need to make this protection from corrosion determines the first operational drawback because flaws may occur in the protective covering of the said tubular support as well as in the area in which the electrode is inserted in the support.

The second drawback is constructional, considering the technological steps necessary for the connection between the tubular support and the electrode as well as for obtaining the said

protective covering.

The third drawback is due to the fact that, no matter the defects presented by the protective dielectric layer of the internal surface of the metallic tank, they leave exposed a metallic surface whose dimension is extremely reduced as to the one exposed by the thermostat sheath and by the armour of the electric resistance on which a good part of the current emitted by the anode is discharged; therefore, such current does not carry out protective functions; moreover, if the anode is sacrificial, it wears out more quickly than required.

The object of the present invention, for a metallic container intended for heating a liquid that can cause the electrochemical corrosion of the said container, specifically for a tank water heater for heating water, since the said container is protected from corrosion by means of an impressed current anode, is to resolve the above-mentioned drawbacks.

A further object of the present invention, for the aforementioned containers, is to prevent the calcareous scales to deposit on the armoured electric resistances.

These and other purposes are achieved with a device protecting from corrosion with impressed currents where the electrode acting as an anode has, according to the invention, the special feasible form resulting from the following description, from the illustrations and from the annexed claims, which form an integral part of the description.

In order to illustrate the invention,

- figure 1 shows a cutaway view, and according to a possible version of the invention, a metallic tank, the boiler of a tank water heater in particular, provided with a closing flange where the thermostat sheath and an armoured electric resistance are mounted, as usual;

- figure 2 shows an enlarged detail of figure 1 for pointing out the details of the electrode according to the invention.

With reference to fig. 1 or 2, they show: a metallic tank 1 to be protected from corrosion, a closing flange 2, usually metallic, of the said tank 1 to which it is fixed by means of several bolts 3; the said flange 2 also acts as a support for the sheath 4 of a thermostat and for an armoured electric resistance 5 that stretch out inside the tank 1; the external metallic armour 5.1 and one of the terminals 5.3 of the armoured electric resistance 5 are indicated; the electric connector 5.2 is welded to one end of the terminal while from the other end branches off the resistive filament 5.4; the sheaths 4 as well as the armoured electric resistances 5 can be more than one. Then the figure displays a generator 6 of impressed currents for the cathode

protection, the first electric cable 7 that connects electrically the negative pole of the said generator 6 with the tank 1 by means of an electric connector 8, the second electric cable 9 that connects the positive pole of the said generator 6 with the metallic armour 5.1 by means of a general fixing element 10 as a clamp or another known proper electrical connecting device; it also displays a general fixing device 11 in dielectric material apt to connect hermetically the resistance 5 to the flange 2 while N indicates the end of the armoured electric resistance 5 that does not supply heat since the resistive filament 5.4 is not present.

With reference to fig. 2, it indicates, apart from elements already defined, a feasible shape of the fixing device 11 obtained, in a removable way, with a bush of dielectric material 11.1, a retaining seal 11.2 and a threaded ring 11.3; however, the fixing device 11 can simply consist of a proper insulating mastic normally on sale.

It is already obvious from the illustrations how, according to the invention, the electrode function for the supply of the impressed currents is carried out simply by the armour 5.1 of the resistance 5 which is assembled electrically insulated as to the tank while it is electrically connected to the positive pole of the generator 6.

The armour must be made of a metal or a metallic alloy that is not subject to electrochemical corrosion at least for the values of potential difference and of current density required for the impressed current cathode protection.

The best materials are titanium in a more or less pure degree or its special alloys that, actually, due to their high resistance to corrosion, are already widely used for making electrodes for impressed current devices; moreover, such materials have also mechanical characteristics suitable for the working processes required by the constructional technology of the armoured electric resistances.

The metallic surfaces plunged in the tank that do not require a protection from corrosion, if and because they are made of stainless material, must be electrically insulated in order to prevent them from absorbing uselessly the current emitted by the anode causing also a so-called "shadow effect" on part of the surfaces that must be protected.

Since the resistance 5, whose armour 5.1 forms the electrode according to the invention, mainly extends very near the sheath 4 of the thermostat, actually the latter may absorb and neutralise the effect of a reasonable amount of the current supplied by the generator 6. In order to avoid this, the said sheath 4 must be mounted on the flange 2 by means of special

devices, not shown in the figures, which ensure the electric insulation from the remaining metallic parts or, more efficiently, it can be entirely covered by a thin layer of dielectric material to avoid undesired electric connections through the sensors contained in it. Similar insulated fixing or insulating treatment may have any other metallic element that cannot be corroded present in tank 1.

The constructional simplification obtained according to the invention is manifest, and the ensuing greater reliability due to the fact that the electrode, as a separate element, has been eliminated since its function is carried out by another element, the armour 5.1, already present and necessary and that has not undergone any constructional change, except for the choice of the most suitable material for the dual capacity.

Another advantage is the electric resistance 5, contrary to what occurs for electrodes with a known feasible shape and assembly systems, it does not absorb part of the current supplied by the electrode, depriving of it the metallic surface to be protected, being itself, on the contrary, the supplying electrode.

However, the invention has also discovered, and this results in a more important advantage that cannot be achieved otherwise, that even in the presence of very hard water, applying a positive electric potential to the armour 5.1 as to the water contained in tank 1, prevents the calcareous scales to deposit on the armour 5.1 eliminating the ensuing drawbacks already discussed and by increasing greatly the life of the resistance.

As already said, the chemical treatment of the surfaces of metallic manufactured items in order to reduce the emission of current from their surface towards an electrolyte in which they are plunged is known; this characteristic can be used for eliminating or reducing considerably the supply of current from some portions of the surface of the armour 5.1. For example, being the end N of the resistance 5 cold, it is not subjected to scales; moreover, from this area N, which generally is in a decentralised position as to the surface of the tank 1 to be protected, it is not necessary nor advisable to emit protection current that otherwise would not be evenly distributed on tank 1; therefore, the emission may be prevented with special surface treatments, chemical treatments in particular, aimed at insulating electrically the surface of the armour 5.1 at the area N so that the impressed current be supplied evenly on the surface of the tank 1, even if the electric resistance 5 is in a mainly decentralised position as to the tank 1.

In conclusion, the fact of assigning the armour 5.1, according to the invention, the function of

electrode of a cathode protection device performs the dual capacity of protecting the tank 1 from corrosion and the resistance 5 from breakage due to overheating, even if such invention allows to balance sufficiently the supply areas of the impressed current.

CLAIMS

1. Device for protecting from corrosion metallic tanks (1) for heating liquids like those using the principle of protection through non-consumable electrode, specifically device for protecting water heaters from corrosion through impressed current cathode protection, characterised in that,

   the part used as an electrode is part of the external surface or armour (5.1) of one ore more electric armoured resistances (5) for heating the liquid contained in the tank (1),

   since the said armour (5.1),

   - is kept electrically insulated as to the other metallic parts of the said metallic tank (1), except for the electric connection to the current generator (6)
   - and is built in a metal or metallic alloy suitable for the production processes of the armoured electric resistances as well as resistant to the electrochemical corrosion.

2. Device according to claim 1), characterised in that the said electrical insulation of the armour (5.1) is obtained by fixing the armoured electric resistance (5) to the supporting device or flange (2) by means of fixing devices (11) in dielectric material consisting of removable elements (11.1, 11.2, 11.3) or dope.
3. Device, according to one or more of the previous claims, characterised in that the said armour (5.1) is made of titanium or a titanium-based metallic alloy.
4. Device, according to one or more of the previous claims, characterised in that in one or more areas of the armour (5.1) the current supply is prevented.
5. Device according to the previous claim characterised in that the said areas of prevention of the current are those (N) in which the armoured electric resistance (5) is without the resistive filament (5.4).
6. Device, according to one or more of the previous claims, characterised in that the current supply in one or more areas of the armour (5.1) is prevented by means of appropriate and known chemical treatments of the said areas.
7. Device, according to one or more of the previous claims, characterised in that the armour (5.1) is electrically connected to the tank to be protected (1) by means of an electric circuit consisting of a generator (6), electric cables (7, 9) and connecting elements (8, 10).

8. Device, according to one or more of the previous claims, characterised in that, any metallic element that cannot be corroded present inside the tank (1) apart from the armours (5.1) acting as electrode, specifically the one or more thermostat sheaths (4) near the armoured electric resistances (5), is electrically insulated by the surrounding electrically conductive means and/or by the liquid contained in the tank (1) by fixing and/or covering with special dielectric materials.

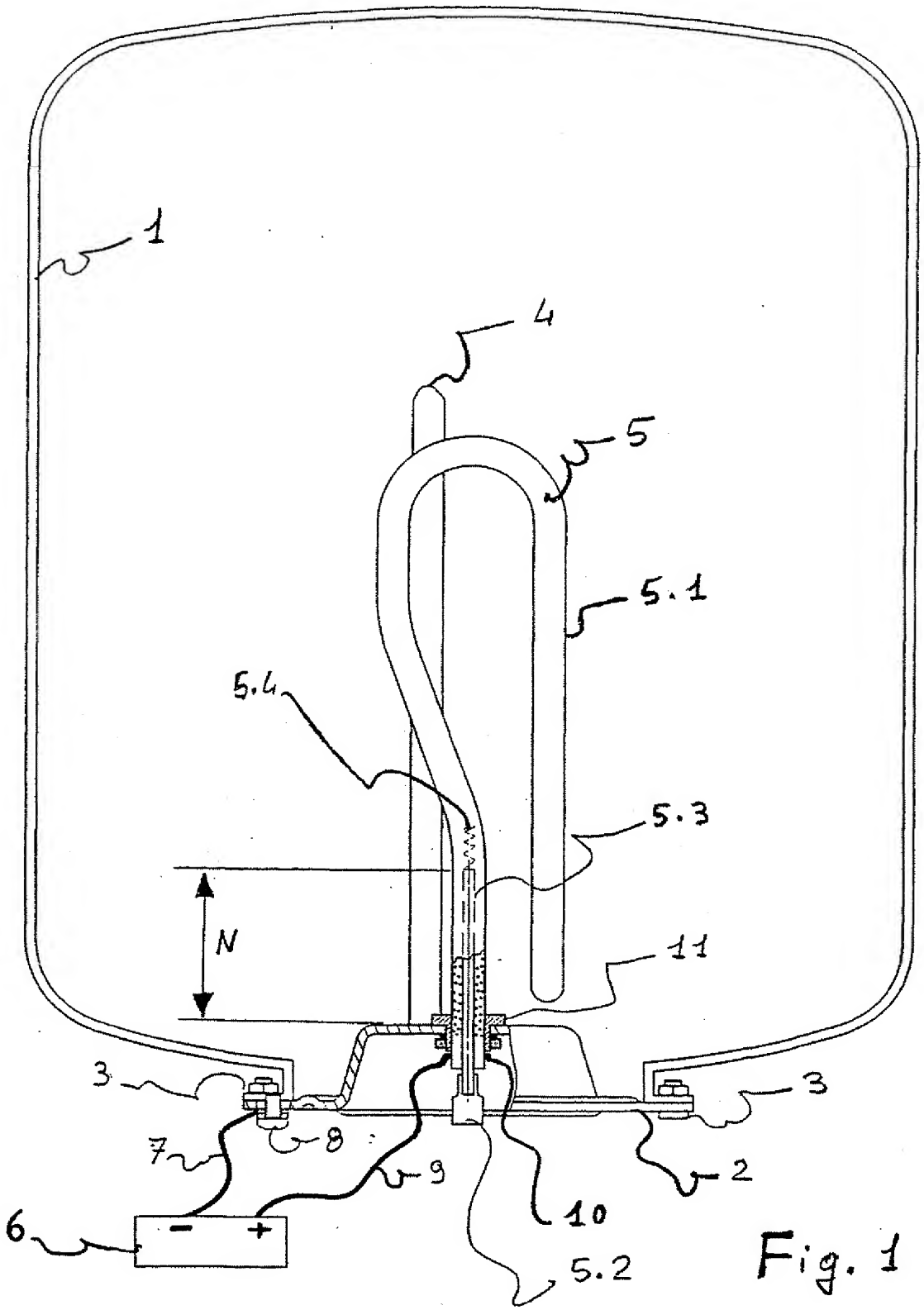


Fig. 1

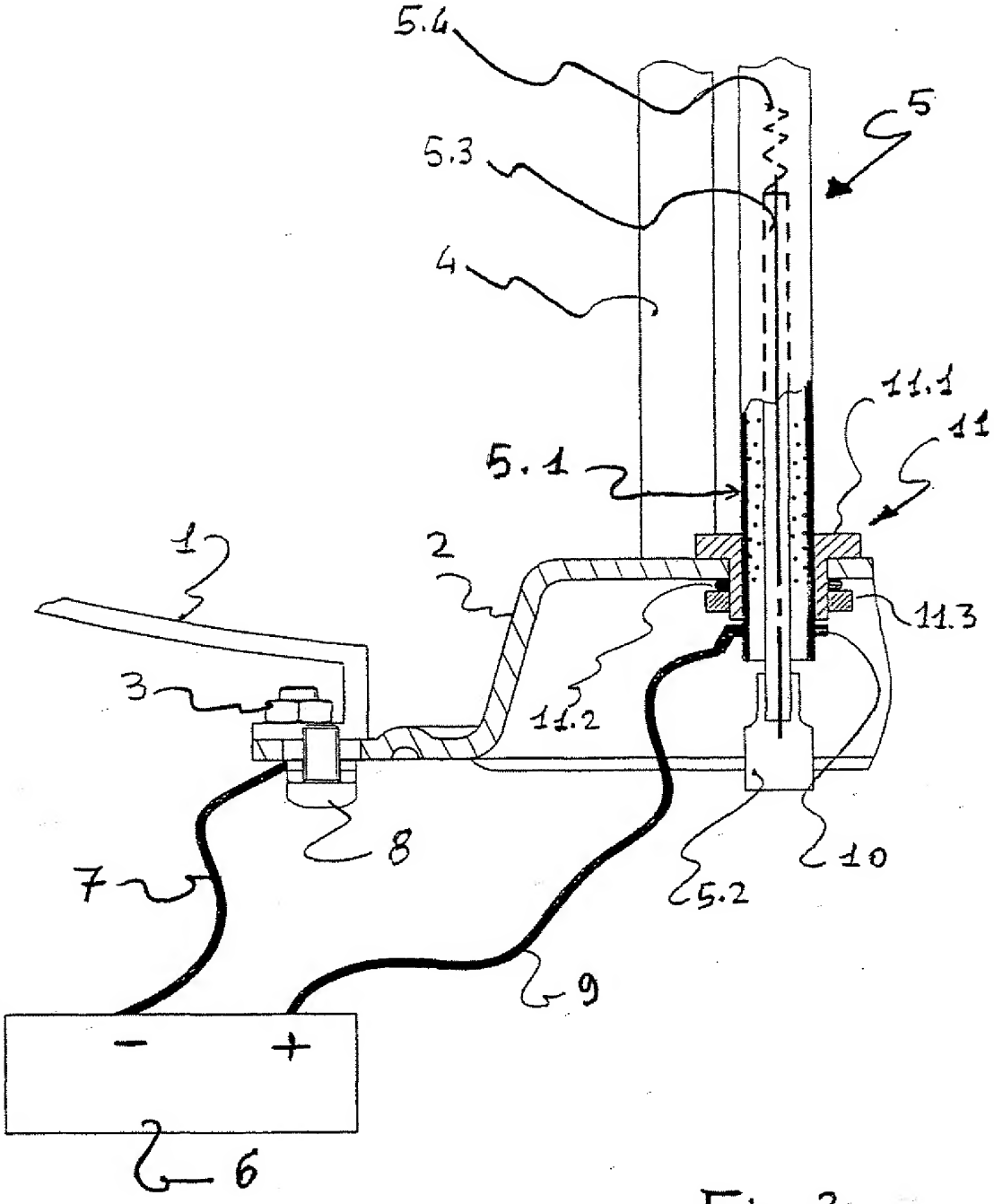


Fig. 2